spectrum: 386 (27.4), M^+; 317 (100), $(M - CF_3)^+$; 262 (6.2), PH_3P^+; 201 (7.3), Ph_2PO^+; 183 (30.7), $(C_6H_4)_2P^+$; 108 (12.4), PhP^+ or $C_4H_3F_3^+$; 77 (8.8), Ph^+; 51 (8.0), $C_4H_3^+$.

CONCLUSIONS

1. Perfluorocarboxylic acid anhydrides and halides undergo the Wittig reaction with stable phosphorus ylides that do not contain an α-hydrogen atom.

2. In contrast to other carbonyl compounds, perfluorocarboxylic acid anhydrides and halides undergo the Wittig reaction with hexafluoroisopropylidenetriethoxyphosphorane.

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ISOMERIZATION OF A PERFLUORO α-LACTAM TO A SUBSTITUTED CARBAMOYL FLUORIDE

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It is known [1] that α-lactams of the I type, which contain an H atom in the β position relative to the carbonyl group, undergo isomerization to amides of α,β-unsaturated acids with cleavage of the C—N bond and migration of β-H to N. This sort of transformation is unlikely for the perfluorinated analog (II) of the α-lactam. In fact, 1-perfluoro-tert-butyl-3,3-bis(trifluoromethyl)aziridin-2-one (II) remains unchanged when it is heated under more severe conditions than in the case of I [2], but it undergoes a different transformation, viz., isomerization to hexafluoroacetone perfluoropivalylimine (III) with cleavage of the C—C bond and migration of the perfluoro-tert-butyl group from N to the carbonyl C atom, under the influence of equimolar amounts to CsF [3].

We have found that α-lactam II is converted almost quantitatively to acid fluoride IV under the influence of catalytic amounts of tertiary amines. This new isomerization can be conceived of as the nucleophilic analog of isomerization of unfluorinated lactams: F^- is split out instead of H^+, characteristic (for α-lactam II) cleavage of the C—C bond occurs instead of cleavage of the C—N bond [3, 4], and the fluoride ion migrates to the carbonyl group (the rate of isomerization increases as the basicity of the amine increases)

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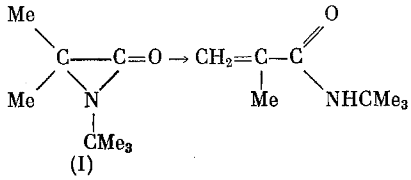
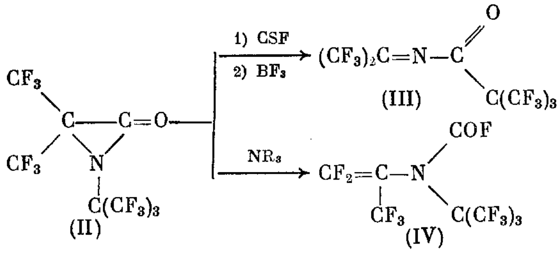
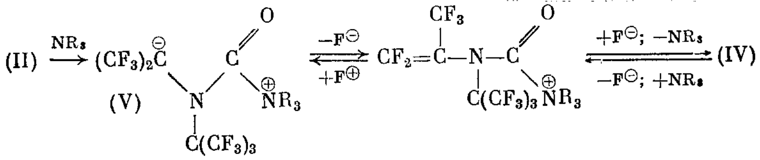


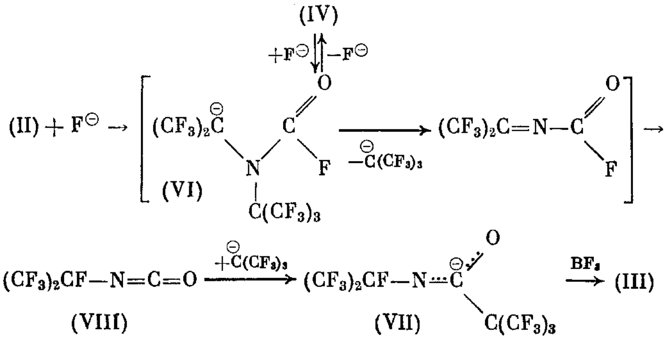


The isomerization of II to IV resembles the isomerization of bis(trifluoromethyl)ketene to perfluoromethacrylyl fluoride [5], except that the three-membered ring is cleaved instead of the C–C bond.

The catalytic role of tertiary amines apparently consists in the fact that the amine, like the fluoride ion [3], attacks the carbonyl carbon atom to give betaine V, which is stabilized by the elimination of F^-, which then replaces NR_3:

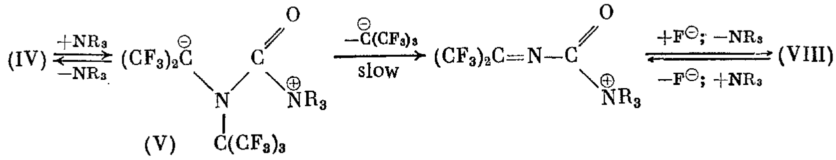


It might be assumed that IV is also formed from II by the action of CsF, but the irreversible migration of the perfluoro-tert-butyl group from the N atom to the carbonyl group shifts the IV ⇌ VI equilibrium to favor the formation of anion VII:



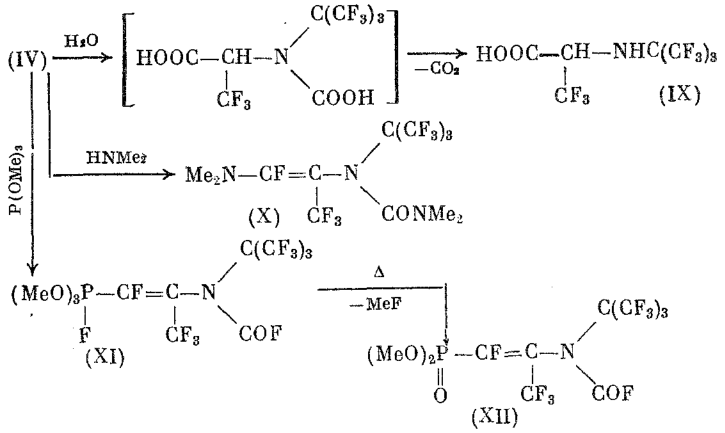
In fact, treatment of acid fluoride IV with an equimolar amount of CsF leads to anion VII (^{19}F NMR spectroscopy). However, both II and IV remain basically unchanged when they are treated with small amounts of CsF and undergo conversion to only a slight degree to anion VII, isocyanate VIII, and perfluoroisobutylene (according to ^{19}F NMR spectroscopy).

The principal reason for the differences in the action of CsF and tertiary amines apparently consists in the fact that CsF bonds with acid fluoride IV and amine III more strongly than tertiary amines and in the fact that the ejection of a perfluoro-tert-butyl anion from betaine V occurs with greater difficulty than from anion VI. However, in the presence of an amine acid fluoride IV nevertheless slowly decomposes to isocyanate VIII, perfluoroisobutylene, and monohydroperfluoroisobutane at ∿20°C.



In the absence of a tertiary amine acid fluoride IV remains unchanged even when it is heated for a long time to 150-200°C. The reactions of IV with water and dimethylamine are realized at the acid fluoride group and the C=C bond to give, respectively, amino acid IX and substituted urea X. Acid fluoride IV does not react with weak nucleophiles such as MeCOOH and benzaldehyde, and only the olefinic bond undergoes reaction with trimethyl phosphite to give a product of "vinyl" substitution, viz., phosphorane XI, i.e., as in the case of perfluoromethacrylyl fluoride [6], the C=C bond proves to be more active than the C=O bond.

Phosphorane XI is stable at ∿20°C; however, it decomposes at 100°C with splitting out of MeF and the formation of primarily phosphonate XII — a product of Arbuzov rearrangement:



Thus phosphorane XI behaves like adducts of trialkyl phosphites with perfluoroisobutylene but not with perfluoromethacrylic acid esters [6].

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded with a Perkin-Elmer R-32 spectrometer (at 90 MHz in the case of the ^1H NMR spectra and at 84.6 MHz in the case of the ^{19}F NMR spectra) with tetramethylsilane and CF_3COOH as the external standards on the δ scale (in parts per million). The IR spectra were obtained with a UP-20 spectrometer. The mass spectra were obtained with a Varian MAT CH-8 spectrometer at an ionizing-electron energy of 70 eV; the m/z values, intensities in percent, and tentative assignments of the intense peaks are given.

N-Perfluoro-tert-butyl-N-perfluoroisopropenylcarbamoyl Fluoride (IV). Eight to ten drops of tributylamine were added to 10 g of α-lactam II, and the mixture was stirred. At the end of the exothermic reaction, the product was distilled in vacuo (3-5 mm) into a trap (—78°C) and fractionated to give 9.3 g (93%) of carbamoyl fluoride IV with bp 117-119°C. Found: C 23.30; F 69.70; N 4.03%. $C_8F_{15}NO$. Calculated: C 23.35; F 69.34; N 3.40%. IR spectrum (ν, cm⁻¹): 1740 (C=C); 1840, 1870 (C=O). ^{19}F NMR spectrum (ppm): —3.3 dq (CF=), —7.1 m (CF=), —12.2 m [$(CF_3)_3C$], —13.4 m (CF_3), —73.6 m (COF), and $J_{CF-CF} = J_{CF-CF_3} = 11.2$ Hz. Mass spectrum: 411 (6) M^+, 392 (13.7) $[M-F]^+$, 342 (0.9) $[M-CF_3]^+$, 314 (2) $[M-CF_2-CF_3]^+$, 264 (22.4) $[M-C_2F_4-COF]^+$, 226 (20) $[M-C_2F_6-COF]^+$, 192 (3) $[M-C_4F_9]^+$, 176 (5.5) $[M-C_3F_9-CO]^+$, 173 (30) $[M-C_4F_{10}]^+$, 142 (6, 7) $[M-C_4F_9-CF_2]^+$, 131 (1.5) $[C_3F_5]^+$, 112 (5.3) $[C_3F_4]^+$, 76 (6.5) $[CF_2CN]^+$, 69 (100) $[CF_3]^+$, 47 (55) $[COF]^+$.

α-Lactam II underwent complete isomerization at 20°C with catalytic amounts of dimethylbenzylamine in 5 h, as compared with 8-10 days with dimethylaniline (according to ^{19}F NMR data).

Reaction of Carbamoyl Fluoride IV with CsF. An equimolar amount of carbamoyl fluoride IV was added to a suspension of freshly calcined CsF in absolute diglyme, as a result of which a solution of the salt of VII was obtained (according to ^{19}F NMR data).

N-Perfluoro-tert-butyl-β,β,β-trifluoro-α-alanine (IX). Several drops of water were added to a solution of 1.5 g of carbamoyl fluoride IV in 2 ml of ether, and the mixture was allowed to stand in a sealed ampul at 20°C for 3 days. The ether solution was dried over $MgSO_4$, the ether was removed by distillation, and the residue was fractionated to give 0.7 g (54%) of alanine IX with bp 65-67°C (3 mm) and mp 67-69°C (from hexane, sublimation). Found: C 23.06; H 0.86; F 62.54; N 3.95%. $C_7H_3F_{12}NO_2$. Calculated: C 23.26; H 0.83; F 63.15; N 3.87%. IR spectrum (ν, cm⁻¹): 1750-1780 (C=O); 2700-3300, 3395, 3430 (NH, OH). PMR spectrum (in MeCN) (ppm): 3.7 broad s (NH), 4.4 m (CH), and 9.9 broad s (OH). ^{19}F NMR spectrum (in MeCN) (ppm): —3.8 m (CF_3) and —7.8 m [$(CF_3)_3Cl$]. Mass spectrum: 361 (0.2) M^+, 342 (1) $[M-F]^+$, 316 (3.6) $[M-COOH]^+$, 292 (1.6) $[M-CF_3]^+$, 246 (28.4) $[M-CF_2-COOH-HF]^+$, 228 (6.6) $[M-CF_4-COOH]^+$, 196 (7.3) $[M-C_2F_4-COOH-HF]^+$, 158 (31.1) $[C_4F_5NH]^+$, 108 (4.2) $[C_3F_3NH]^+$, 96 (6.1) $[C_2F_3NH]^+$, 91 (4.2) $[C_2H_2FNO_2]^+$, 69 (100) $[CF_3]^+$, 51 (9) $[CF_2H]^+$, 45 (28) $[COOH]^+$, 28 (91) $[CO]^+$.

N-(1-Trifluoromethyl-2-fluoro-2-dimethylaminovinyl)-N-perfluoro-tert-butyl-N',N'-dimethylurea (X). A 1-ml sample of dry Me_2NH was passed with cooling and stirring into a solution of 0.7 g of carbamoyl fluoride IV in 2 ml of absolute ether, after which the mixture was stirred for 1 h, and the precipitate was removed by filtration. Workup of the filtrate gave 0.4 g (51%) of urea X with mp 104-106°C (from hexane, sublimation). Found: C 31.45; H 2.50; F 52.89; N 9.15%. $C_{12}H_{12}F_{13}N_3O$. Calculated: C 31.23; H 2.60; F 53.57; N 9.11%. IR spectrum (ν, cm^{-1}): 1660 (C=C) and 1720 (C=O). PMR spectrum (in MeCN) (ppm): 2.8 s (Me_2NCO), 2.9 d (Me_2NCF), J_{H-F} = 2 Hz. ^{19}F NMR spectrum (in MeCN) (ppm): —13.5 dq [$(CF_3)_3C$], —17.3 m (CF=), —20.8 m (CF_3), $J_{CF_3-C(CF_3)_3}$ = 3.7, $J_{CF-(CF_3)_3}$ = 10.3 Hz.

2-(N-Perfluoro-tert-butyl-N-fluorocarbonylamino)tetrafluoropropenyltrimethoxyphosphorane (XI). A 0.3-g sample of trimethyl phosphite was added with stirring and cooling to 1.5 g of carbamoyl fluoride IV. After 1 h, fractionation gave 1.2 g (92%) of phosphorane XI with bp 55-56°C (0.01 mm). Found: P 5.84%. $C_{11}H_9F_{15}NO_4P$. Calculated: P 5.79%. IR spectrum (ν, cm^{-1}): 1620 and 1860. PMR spectrum (ppm): 3.7 d (Me), J_{Me-P} = 15 Hz. ^{19}F NMR spectrum (ppm): +0.9 broad d (PF), —1.3 dm (CF=), —13.5 m [$(CF_3)_3C$], —18.5 m (CF_3), —73.6 m (COF), J_{P-F} = 845, J_{CF-P} = 71.2 Hz.

Dimethyl 2-(N-Perfluoro-tert-butyl-N-fluorocarbonylamino)tetrafluoropropenylphosphonate (XII). A 3.3-g sample of phosphorane XI was heated at 120-130°C for 0.5 h, after which fractionation gave 1.4 g (45%) of phosphonate XII with bp 53-55°C (0.03 mm). Found: C 23.94; H 1.21; F 52.76; P 6.28%. $C_{10}H_6F_{14}NO_4P$. Calculated: C 23.95; H 1.19; F 53.09; P 6.18%. IR spectrum (ν, cm^{-1}): 1640 (C=C); 1830, 1970 (C=O). PMR spectrum (ppm): 4.0 d (Me), J_{Me-P} = 12.4 Hz. ^{19}F NMR spectrum (ppm): +15.8 dm (CF=), —13.1 m [$(CF_3)_3C$], —14.2 m (CF_3), —76.2 m (COF), J_{CF-P} = 84.5 Hz.

Reaction of Carbamoyl Fluoride IV with MeCOOH and Benzaldehyde. When equimolar amounts of MeCOOH (6 h) or benzaldehyde (50 h) were heated (140-150°C) with carbamoyl fluoride IV, the latter remained unchanged (according to the ^{19}F NMR spectra).

CONCLUSIONS

1. Under the influence of tertiary amines 1-perfluoro-tert-butyl-3,3-bis(trifluoromethyl)aziridin-2-one undergoes isomerization with cleavage of the ring C—C bond and migration of a fluoride ion to the carbonyl group.

2. In the reaction of N-perfluoro-tert-butyl-N-perfluoroisopropenylcarbamoyl fluoride with trimethyl phosphite the C=C bond is more electrophilic than the acid fluoride group.

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